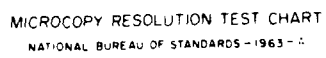MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

OFFICE OF NAVAL RESEARCH

Contract No. N00014-84-C-0699

TECHNICAL REPORT NO. 2

A CLASS OF NARROW BAND GAP SEMICONDUCTING POLYMERS

by

Samson A. Jenekhe
Physical Sciences Center, Honeywell Inc.
Bloomington, Minnesota 55420

DTIC
ELECTE
JUL 7 1986
S   B
D

AD-A169 507

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT DISTRIBUTION STATEMENT A Approved for public release Distribution Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical REport No. 2	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Honeywell Inc. Physical Sciences Center	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION ONR
6c. ADDRESS (City, State and ZIP Code) 10701 Lyndale Avenue South Bloomington, Minnesota 55420		7b. ADDRESS (City, State and ZIP Code)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable) ONR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-C-0699

8c. ADDRESS (City, State and ZIP Code) 800 North Quincy Str-et Arlington, VA 22217	10. SOURCE OF FUNDING NOS.			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.

11. TITLE (Include Security Classification) A Class of Narrow Band Gap SemiConducting Polymers

12. PERSONAL AUTHOR(S) Samson A. Jenekhe

13a. TYPE OF REPORT Publication	13b. TIME COVERED FROM ___ TO ___	14. DATE OF REPORT (Yr., Mo., Day) June 25, 1986	15. PAGE COUNT

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	Semiconducting polymers; alternating aromatic/quinonoid polymers; narrow band gap organic semiconductors.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A novel class of conjugated polymers containing alternating aromatic and quinonoid segments in the main chain is described. Some of the polymers exhibit intrinsic band gaps as low as 0.75 ev, the smallest known value of the band gap of organic polymers. The idea that introduction of quinonoid character into a polymer main chain could lower the band gap is experimentally demonstrated and the effect described in terms of molecular parameters and bond-length alternation.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Kenneth J. Wynne	22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE. Unclassified

A CLASS OF NARROW BAND GAP SEMICONDUCTING POLYMERS

Samson A. Jenekhe

Honeywell Inc., Physical Sciences Center

Bloomington, Minnesota 55420 (U.S.A.)

Scientific interest in electrically conducting polymers and conjugated polymers in general has been widespread, and continues to grow, among workers in polymer science, chemistry, condensed matter physics, materials science, and related fields since the discovery of doped conductive polyacetylene.[1,2] Numerous doped conducting organic polymers with conductivity spanning the insulator to near metallic range ($\sim 10^{-15}$ to 10^3 ohm^{-1} cm^{-1}) are now known.[1-13] Of prime importance and fundamental interest in the continuing experimental and theoretical search for new conducting, and perhaps superconducting, polymers is achievement of small or vanishing semiconductor band gap (E_g) which governs the intrinsic electronic, optical, and magnetic properties of materials. Existence of a finite E_g in conjugated polymers is thought to originate principally from bond-length alternation which is related to the Peierls instability theorem for one-dimensional metals.[14-16] Here we describe a novel class of conjugated polymers containing alternating aromatic and quinonoid segments whose members exhibit intrinsic band gaps as low as 0.75 ev, the smallest known value of E_g for organic polymers.

Among conjugated polyenes, polyenynes, and related polymers, polyacetylene (PA), $(-CH=CH-)_m$, has the smallest band gap with a value of 1.5 ev.[3] Among the aromatic and heteroaromatic conjugated polymers, polythiophene (PT) (Figure 1, A with X = S) has the smallest band gap with a value of ~ 2.1-2.2 ev.[8,13] In the search for narrower band gap

polymers, the strategy of substitution on existing main chain polymers or formation of copolymers has not been successful to date. An important exception is the annelated 3,4-benzo derivative of polythiophene, i.e polyisothianaphthene (PITN), which has an E_g value as low as 1.13 ev.[13] Wudl et. al. have attributed the difference in E_g values between PT and PITN to contribution of quinonoid resonance structure (Figure 1, B) in the case of PITN and a lack of such contribution in PT[13]. We have argued elsewhere that a large part of the ~1 ev difference in E_g values of PT and PITN is attributable to coplanarity of polymer repeating units in PITN and its lack in PT.[17] However, introduction of quinonoid character into the main chain of an aromatic conjugated polymer can be expected to lower the band gap. In fact, we have already observed a somewhat similar effect in polycarbazoles.[10] Also, Bredas has recently shown theoretically via Valence Effective Hamiltonian (VEH) calculations that as quinonoid structure is introduced into polythiophene geometry (Figure 1, A,B) E_g decreases linearly with increasing quinonoid character.[18]

Figure 1C shows a class of heteroaromatic conjugated polymers we designed to incorporate aromatic and quinonoid segments in the main chain and hoped would lead to small E_g values. There are several interesting general features of this class of polymers. (i) The quinonoid character is given in terms of integer molecular parameters (x,y) which could be subject to synthetic manipulation. Neglecting possible end group effects, the fraction of quinonoid character $Q = y/(x+y)$. Thus, $Q = 0$, 1/2, 2/3, 3/4, 4/5, etc. when $y/x = 0$, 1, 2, 3, 4, etc; and $Q = 1/3$, 1/4, 1/5, 1/6, etc. when $y/x = 1/2$, 1/3, 1/4, 1/5, etc. The limiting cases of $Q = 0$ ($y = 0$ or $x \rightarrow \infty$) and $Q = 1$ ($x = 0$ or $y \rightarrow \infty$) essentially correspond respectively to polymers with chain structures A and B (Figure 1). The hypothetical polymer B, relative to A and polymers of

- 2 -

intermediate compositions, has a lower but nonetheless finite E_g[18]. The parameter Q could in principle be related to bond-length alternation Δr ($=d_1-d_2$) by some function $f(\Delta r)$, where d_1 and d_2 are the C-C and C=C bond lengths respectively. The value of Q when $\Delta r = 0$ and of Δr when E_g is minimum would be of interest in understanding the origin of E_g in conjugated polymers. (ii) The ground state structure of this class of polymers is two-fold degenerate in the sense of trans-PA, when Q = 1/2 or x = y = 1, 2, 3, 4, etc. In fact, when x = y= 0 (Q =0) and R = H we obtain polyacetylene; however, the uniqueness of polyacetylene is preserved by its Q = 0 value. Soliton excitations have been postulated for trans-PA on the basis of its degenerate ground state structure.[19] So, soliton excitations may be anticipated in the degenerate or symmetric (Q = 1/2) polymers of Figure 1C. However, it is unclear to what extent a finite Q will influence such excitations relative to trans-PA. (iii) If the hetero-atom (X) is neglected the polymer backbone is essentially an alternating copolymer of trans-cisoid and cis-transoid forms of polyacetylene. (iv) Doping in aromatic (e.g. poly p-phenylene) and heteroaromatic (Figure 1A) polymers leads to polarons and bipolarons as the charged species presumably by increasing the quinonoid character (Q) of the chain.[20-21] Since the present class of polymers already have Q>0, it is uncertain how much more, if any, quinonoid character can result from doping. (v) As macromolecules, this class of polymers has an unusual "expandable" constitutional repeating unit (CRU) consisting of aromatic and quinonoid segments. Conceivably, a very high molecular weight material (say 10^7) could result from a small chain length (say m = 1), simply by increasing x and y! The synthetic feasibility of such materials is another matter, but this suggests that the electronic and optical properties would be more sensitive to x and y than the polymer chain length m. These features and questions certainly warrant a detailed theoretical investigation.

The proposed polymers Figure 1C wherein x = y = 1, 2, or 3 (Q = 1/2) have been experimentally realized for various X and R by a two-step synthetic technique shown in Scheme 1. First, nonconjugated precursor polymers containing alternating sp^3 carbon atom (-CRH-) and heteroaromatic conjugated units D were synthesized by condensation polymerization of the appropriate monomer, dimer, or trimer (Ia) with aldehydes (Ib), where D is 2,5-thiophenediyl, 5,5',α-bithiophenediyl, 5,5",α-terthiophenediyl, etc. Second, the presursors (II) were converted to the conjugated polymers with alternating aromatic and quinonoid segments (III) by oxidative elimination of the bridge hydrogens. This two-step synthesis could also be used to achieve the non-symmetric polymers of Figure 1C, i.e. other than Q = 1/2. Note that the basic linear structure of the conjugated polymers (III) is the same as that of the precursors (II); the structure of the precursors (II) was readily established by infrared spectra. The precursor polymers have been characterized by infrared and electronic spectra, elemental analysis, molecular weight studies, and thermal analysis. Evidence of the elimination of the bridge hydrogens is provided principally by infrared and electronic spectra; insolubility of polymers III compared to polymers II provides an additional proof of elimination. Details of the syntheses of the conjugated polymers and their precursors are described elsewhere.[17,22-23] The smallest band gaps were obtained when X = S. Also, E_g values were less sensitive to the side group R.

Figure 2 shows the optical absorption spectra for a thin film (~0.1-0.2 μm) of a polymer where R = phenyl, X = S and x = y = 3. Curve 1 is the optical absorption spectrum of the polymer precursor, poly(5,5',α-terthiophenediyl benzylidene) (PTTB). Curve 2 is that of a conjugated derivative (Figure 1C) which has an E_g of 0.83 ev (1500 nm) and corresponds to the product of elimination after 7.1 min of reaction. Upon exhausive elimination (curves 2-10) the band gap narrows to a constant value of 0.75 ev (1650 nm). Similar results of band gap narrowing to a constant value during elimination have been obtained for x = y = 1 and 2: y = 1, E_g = 1.1 ev; y = 2, E_g = 0.83 ev.

The band gap as a function of y is shown in Figure 3 for X = S and x = y. The point shown at y = 0 is that of <u>trans-PA</u>; this is because the general polymer repeating unit shown on Figure 3 contains 8y+2 carbon atoms in the main chain which naturally reduces to polyacetylene in the limit y = 0. It is clear that the asymptotic value of $E_g(y)$ is of order 0.7 ev which is already closely approached at y = 3.

As expected the proposed polymers do exhibit narrow band gaps. Although the quinonoid character via the parameter Q qualitatively explains why E_g is smaller in this class of polymers compared to PT, it does not explain why the band gap decreases with y at a constant Q as observed. If a linear relationship holds between E_g and Q it will be approximately E_g = 2.2 - 2.05 Q, using the band gap of PT (2.2 ev, Q = 0) and the calculated 0.15 ev for Q = 1 by Bredas.[18] An expected E_g value of 1.18 ev at Q = 1/2 is close to 1.1 ev found for y = 1, but then the other values of the band gap at Q = 1/2 cannot be explained by this linear equation at all. We believe this is due to the degeneracy of the case Q = 1/2. An explanation of both the generally small band gaps in this class of polymers and specifically E_g decrease with y can be given in terms of the more primitive concept, <u>bond-length alternation</u> Δr. E_g decrease with y is consistent with bond alternation decrease with expansion of the polymer repeating unit. From the theoretical calculations of Grant and Batra for <u>trans-PA</u>[15] and Bredas for PT[18] a linear relationship of the form $E_g = E_g^o + b \Delta r$ appears to hold. We have obtained the same value of b = 11.50 ev/Å from the two different calculations.[15,18] However, E_g^o = 0 for <u>trans-PA</u>[15] and E_g^o = 0.705 ev for PT[18]. This linear equation and the observed band gaps give estimated bond alternations of 0.034, 0.011 and 0.004 Å for y = 1, 2 and 3 respectively compared to 0.13 Å for PT. It will be interesting to compare these estimated bond alternation values with those computed or measured directly. Even from these estimates it is clear that nearly uniform bond lengths are attained at y = 3 and yet the band gap is as high as 0.75 ev due primarily to E_g^o. Existence of a finite E_g^o further distinguishes aromatic and heteroaromatic conjugated polymers from polyenes[18] and raises the question of its origin since only the amount above E_g^o can be attributed to bond alternation. Narrower band gaps would inply

- 5 -

<u>negative</u> bond alternation ($\Delta r < 0$) in which carbon-carbon double bonds are longer than single bonds. In principle, as the calculations of Bredas suggest,[18] the proposed heteroaromatic polymers (Figure 1C), wherein $Q \longrightarrow 1$ could exhibit band gaps smaller than E_g^o but experimental realization of such members of this class of polymers remains to be seen.

Obviously, other heteroaromatic or aromatic polymers with structures similar to Figure 1C and hence similar properties can be expected when the heteroaromatic units, $(C_4H_2X)_{y,x}$, are replaced by phenyl (Ph), p-phenylene oligomers, or other groups capable of both aromatic and quinonoid bonding structures. In this regard, it is interesting to note that after we had already experimentally realized the polymers described here we became aware of the theoretical work of others predicting a narrow band gap for a structurally related <u>hypothetical</u> (not yet synthesized) polymer. Boudreaux <u>et</u>. <u>al</u>. have calculated a band gap of 1.17 ev and predicted existence of soliton excitations in poly p-phenylenemethine, $(-Ph-CH=Ph=CH-)_m$.[24]

In summary, a novel class of tunable narrow band gap conjugated polymers has been described and some of its members have been experimentally realized. The observed band gap of 0.75 ev is the smallest known value for organic polymers. The idea that introduction of quinonoid character into a polymer main chain could lower the band gap is thus experimentally demonstrated and the effect qualitatively described in terms of molecular parameters and bond-length alternation. Studies of the electronic and optical properties of the novel polymers are in progress.

REFERENCES

1. Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C. K. and Heeger, A.J. _J. Chem. Soc. Chem. Commun._, 578(1977).

2. Chiang, C.K., Fincher, Jr., C.R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E.J., Gau, S.C. and MacDiarmid, A.G. _Phys. Rev. Lett._ 39, 1098-101(1977).

3. Chien, J.C.W. _Polyacetylene: Chemistry, Physics and Materials Science_, Academic Press: Orlando, FL, 1984.

4. Ivory, D.M., Miller, G. G., Sowa, J.M., Shacklette, L.W., Chance, R.R. and Baughman, R.H. _J. Chem. Phys._ 71, 1506-7(1979).

5. Clarke, T.C., Kanazawa, K.K., Lee, V.Y., Rabolt, J.F., Reynolds, J.R. and Street, G.B. _J. Polym. Sci.: Polym. Phys. Ed._ 20, 117-30(1982).

6. Diaz, A.F., Kanazawa, K.K. and Gardini, G.P. _J. Chem. Soc. Chem. Commun._, 635(1979).

7. Kanazawa, K.K., Diaz, A.F., Gardini, G.P., Gill, W.D., Grant, P.M., Kwak, J.P. and Street, G.B. _Synthetic Metals 1_, 329-36 (1980).

8. Tourillon, G. and Garnier, F. _J. Electroanal. Chem 135_, 173-8 (1982); _ibid, 161_, 407-14(1984).

9. Wellinghoff, S.T., Kedrowski, T., Jenekhe, S.A. and Ishida, H. _J Phys. Colloq._ 44, 677-81(1983).

10. Jenekhe, S.A., Wellinghoff, S.T. and Deng, Z. _Synthetic Metals 10_, 281-292(1985).

11. Jenekhe, S. A., Wellinghoff, S.T. and Reed, J. F. _Mol. Cryst. Liq. Cryst. 105_, 175-189(1984).

12. Greene, R.L. and Street, G.B. Science 226, 651-656(1984).

13. Wudl, F., Kobayashi, M., Colaneri, N., Boysel, M. and Heeger, A. J. Mol. Cryst. Liq. Cryst. 118, 199-204(1985).

14. (a) Peierls, R. E. Quantum Theory of Solids, Oxford Univ. Press: London, 1955; pp. 108.

    (b) Ovchinnkov, A.A., Ukrainskii, I.I. and Krentsel, G.V. Sovient Phys. Uspekhi 15, 575-591(1973).

15. Grant, P.M. and Batra, I.P. Solid State Commun. 29, 225-229(1979).

16. Simon, J. and Andre, J.-J. Molecular Semiconductors, Springer-Verlag: New York, 1984, pp. 166-173.

17. Jenekhe, S.A. Submitted to Macromolecules.

18. Bredas, J.L. Mol. Cryst. Liq. Cryst. 118, 49-56(1985).

19. Su, W.P., Schrieffer, J.R. and Heeger, A,J. Phys. Rev. B. 22, 2099-2111 (1980); Phys. Rev. Lett. 42, 1698-1701(1979).

20. Bredas, J.L., Themans, B., Andre, J.M., Chance, R.R. and Silbey, R. Synthetic Metals 9, 265-274(1984).

21. Bredas, J.L., Chance, R.R. and Silbey, R. Phys. Rev. B 26, 5843-5854(1982).

22. Jenekhe, S.A. Submitted to Macromolecules.

23. Jenekhe, S.A. To be submitted to Macromolecules.

24. Boudreaux, D.S., Chance, R.R., Elsenbaumer, R.L., Frommer, J.E., Bredas, J.L. and Silbey, R. Phys. Rev. B 31, 652-655(1985).
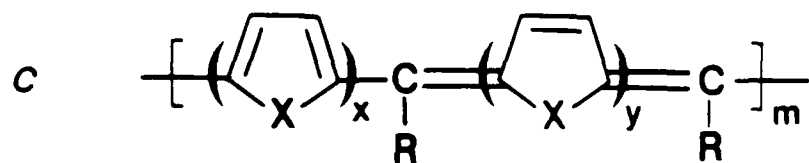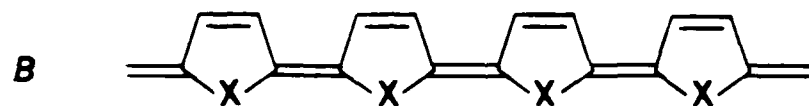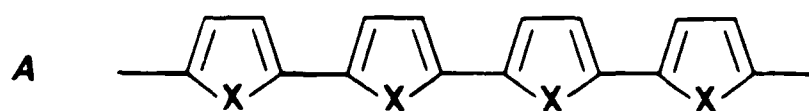
FIGURE CAPTIONS

Figure 1.   A. Aromatic ground state structure of heteroaromatic polymers (X=S, polythiophene; X=N-H, polypyrrole, etc.)   B.   Quinonoid ground state structure of heteroaromatic polymers of A.   C.   Ground state structure of novel tunable narrow band gap conjugated polymers containing alternating aromatic and quinonoid segments, some of which exhibit the smallest E_g values known for organic polymers.

Figure 2.   Optical absorption spectra of thin films of precursor PTTB (1) and conjugated derivatives (2-10) which are the Polymers in Figure 1C.

Figure 3.   The band gap $E_g(y)$ of the polymers in Figure 1C wherein X = S, R = Ph and x = y.   The E_g value at y = 0 is that of trans-PA.
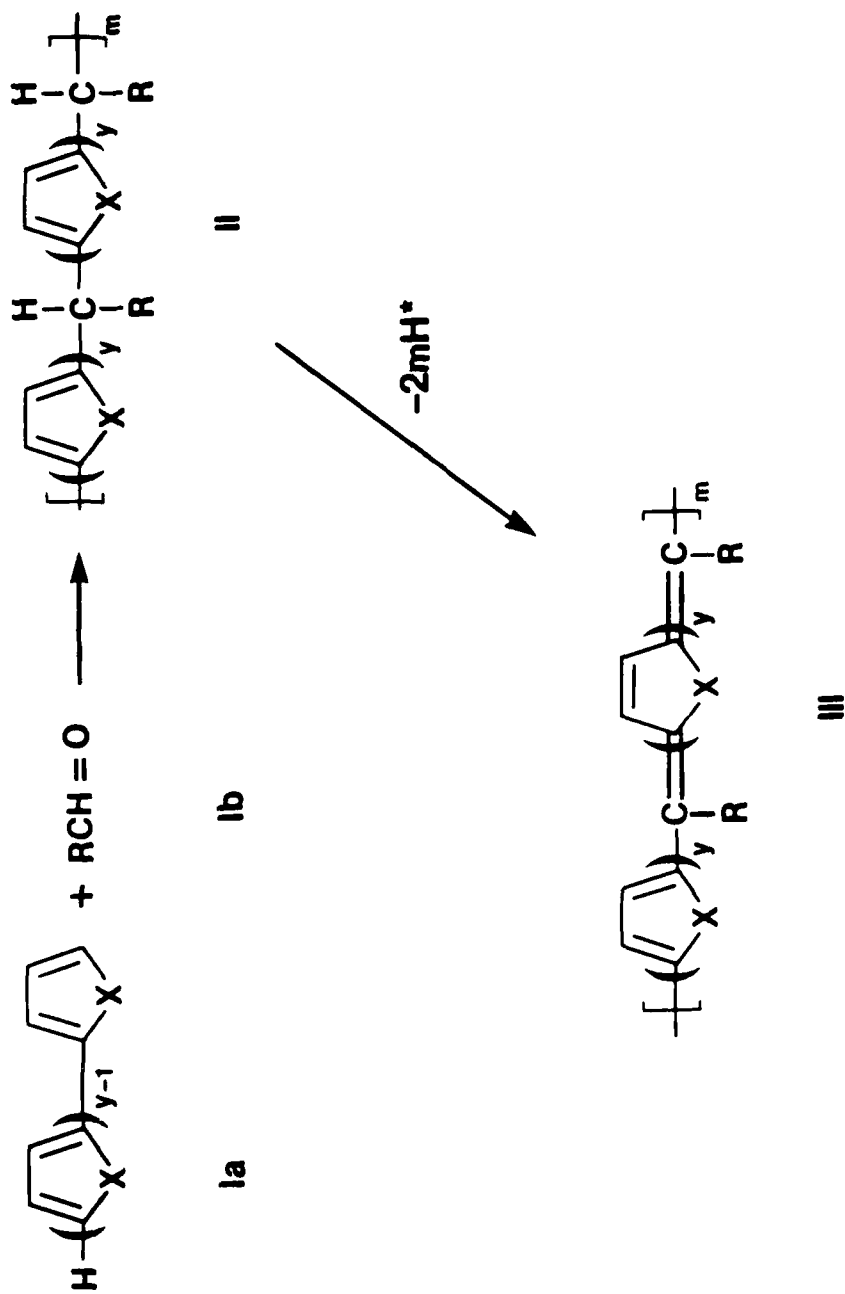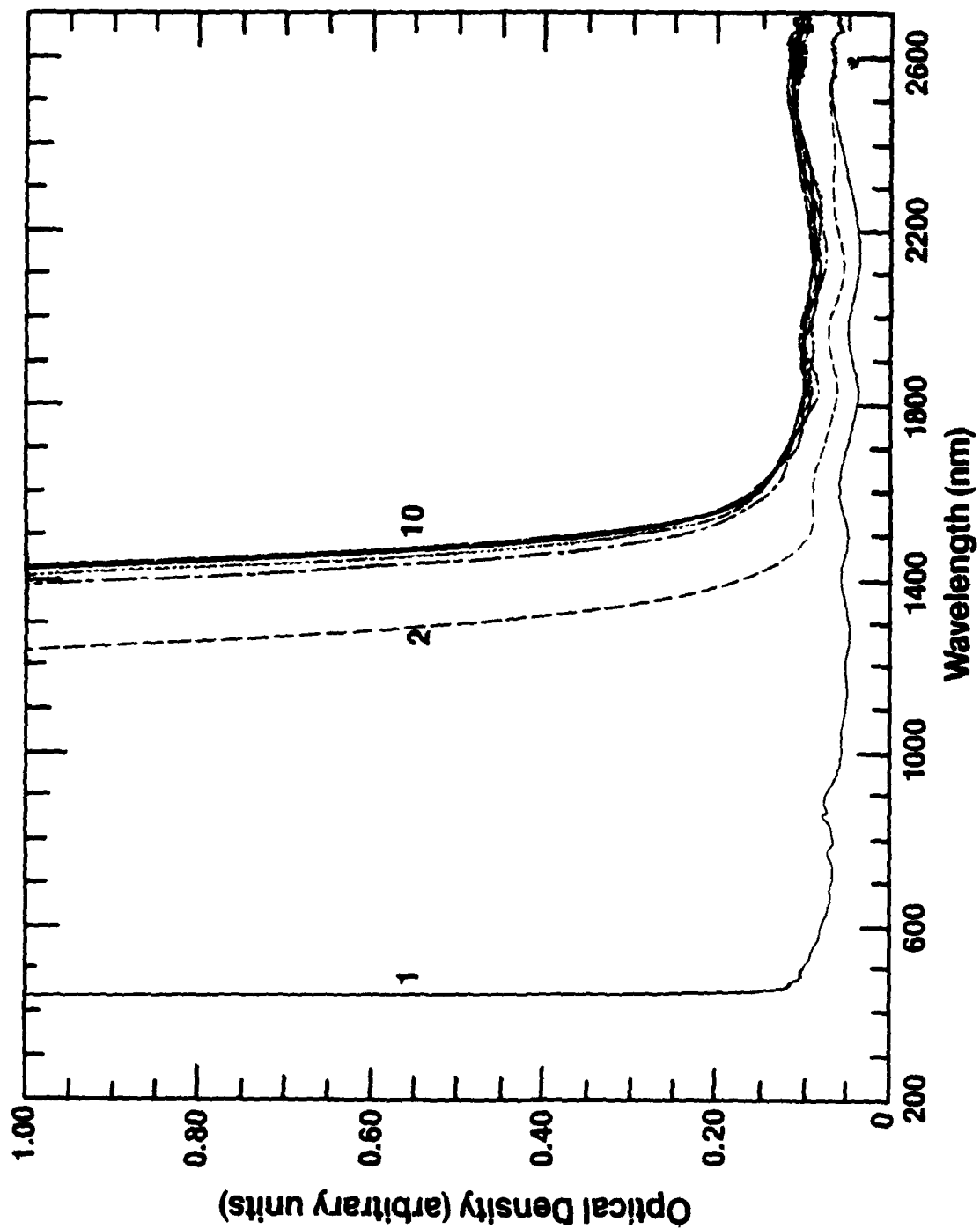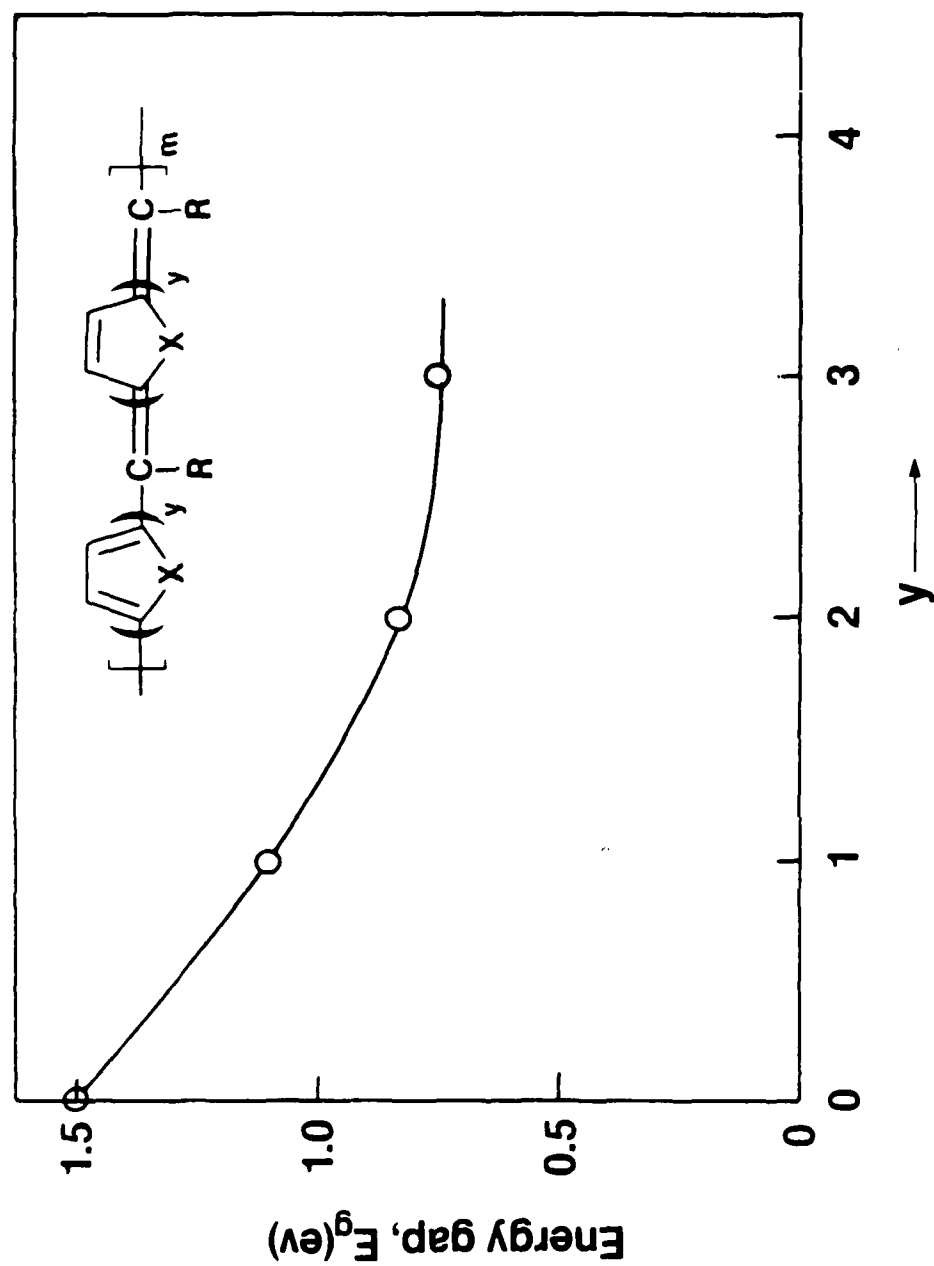
Fig. 1

860562

SCHEME 1

860608

Figure 2

8602814

Figure 3

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

END

DTIC

8-86